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Study the effect of alpha particle fluences on the morphology and optical properties of poly-aniline in nano-scale

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Abstract: *Poly-aniline is one of the most important conducting polymers. The poly-aniline has many applications in the electronic fields such as batteries, sensors, controlling systems and organic displays. It is good environmental stability, easy conductivity control and cheap production in large quantities. In this study poly-aniline samples in nan-structure were irradiated with α- particles with different fluences (1.16 x 10^8- 1.20 x 10^9 alphas/ cm^2) and constant energy (5.32±0.23 MeV). The damage is almost regular along the path length of alpha particles in poly-aniline samples. The modifications in the morphology and optical properties induced by the radiation were measured. It was found a strong correlation between absorbance and the alpha particle fluences at wavelength 600 nm for the samples after irradiations. Also, the results showed increase the number of carbon atoms per cluster in the poly-aniline samples after irradiations.*
Keywords: *Poly-aniline, Alpha particles, band gap energy, cluster size*

I. Introduction

Conducting polymers is a prospective class of new materials that combine solubility, process ability, and flexibility of plastics with electrical and optical properties of metals and semiconductors [1]. These conducting polymers exhibit the unusual electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity [2] due to the presence of extended π-conjugated systems along the polymeric chain [3]. Poly-aniline (PANI) is one of the most important conducting polymers because of excellent electrical properties, electrochemical, electro-rheological. These properties found potential applications in the electronic fields such as batteries, sensors, controlling systems and organic displays [4-7] because of its facile synthetic process, good environmental stability, easy conductivity control and cheap production in large quantities. Poly-aniline can be found in one of three idealized oxidation states: leucoemeraldine $(C_6H_4NH)_n$, emeraldine $(\{[C_6H_4NH]_2[C_6H_4N]_2\}_n)$ and pernigraniline $(C_6H_4N)_n$. Emeraldine base is regarded as the most useful form of poly-aniline due to its high stability at room temperature and the fact that, upon doping with acid, the resulting emeraldine salt form of poly-aniline is highly electrically conducting. But leucoemeraldine and pernigraniline are poor conductors, even when doped with an acid [8-9]. When an ionization radiation passes through a polymeric material, ionization and excitation for molecules of the material are produced [10]. These lead to breaking of original bonds, chain scission, radical formation and cross-linking in polymeric material [11-12]. Scission and cross-linking not only depend upon polymer structure but also upon the energy deposited per unit track length (LET) [13-15]. This, in turn, tends to modify the structure and optical properties of polymers [16-17]. Clusters (number of carbon atoms per cluster) be formed along alpha particle tracks. These clusters supposed to be carriers of electrical conductivity in ion irradiated polymers and influence the optical properties [18]. In the present study, the effect of alpha particle fluences (1.16 x 10^8- 1.20 x 10^9 alphas/ cm^2) and constant energy (5.32±0.23 MeV) on the structure and optical properties of PANI thin films on glass substrate has been investigated.

II. Experimental techniques

2.1. Production of PANI samples

A 0.1 M ammonium persulfate (APS) was dissolved in 50 mL water and kept for 1 h at room temperature. Also, a 0.1 M aniline monomer was prepared in 50 mL water and also kept for 1h at room temperature. To obtain high yield and massive production, PANI was deposited on glass substrate by rapid mixing of the reactants.

2.2. Irradiation process

Holder collimator with a certain height was used to verify normal irradiation for the poly-aniline (1.00 x 1.00 cm^2 x 20 nm) in air by α-particles through a collimator holder at Beni-Suef University, Egypt [19]. The density of poly-aniline was 1.245 g/cm^3. The energy of alpha particle that emerged from the collimator was

determined using a surface barrier detector. The height of the collimator would reduce the energy of 5.486 MeV α-particles which emitted from ^{241}Am- source to 5.32±0.23 MeV.

The incident flux (ϕ) was calculated by the following equation:

$$\phi = \frac{A}{4\pi r^2} \quad (1)$$

Where A is the activity of the ^{241}Am- source in Bq and r is the source-detector distance in centimeters.

The fluence (Φ), the total number of α- particles emitted from the collimator and incident on CR-39 per unit area in a certain irradiation time (t), is:

$$\Phi = \varphi t \quad (2)$$

The irradiations were verified at irradiation times 6.50, 41.00, and 71.00 h. The corresponding fluences according to equation (2) were 1.16 x 10^8, 7.48 x 10^8 and 1.2 x 10^9 alphas /cm^2, respectively. The error in the fluence was 1604 alpha/cm^2.

2.3. Morphology measurements

A field emission scanning electron microscope (FE-SEM), (Model: Leo Supra 55, 1nm resolution, USA) was used to characterize the morphology of the PANI films before and after irradiations.

2.4. Optical absorption spectra

The optical spectra of the virgin and irradiated PANI films were measured by using UV-VIS-NIR spectrophotometer (Shimadzu UV-1601 PC, Japan) in the wavelength range of 300-800 nm).

III. Results and discussion

When energetic alpha particles penetrate the medium, they create damage along the particle trajectory. According to the SRIM program calculations [20], the projected range of 5.32 MeV alpha particles in PANI samples was calculated to be 33.13 μm and the LET was 10.54 eV/Å. The thickness of the PANI samples (20 nm) is small compared with the projected range. According to the Bragg curve (the curve consists of a flat region known as the plateau, after which the LET rises up to its peak value in a region called the Bragg peak, the region of maximum energy transfer), LET is in the flat region. Therefore, the damage is almost regular along the trajectory of alpha particles in PANI samples. The overlapping tracks and the density of the damage (track density) may increase with increasing the irradiation time or fluence of alpha particles. These, in turn, change the physical and chemical properties of the PANI samples.

3.1. PANI morphology

Figure 1 shows top-view SEM images of PANI thin films of the virgin and irradiated samples with different irradiation times or fluences of alpha particles. Smooth and uniform thin film of virgin PANI sample is deposited on the glass substrate for 20 min, as shown in Figure 1(a). The PANI sample irradiated with alpha particles at 6.50 h showed some nanoparticles aggregation as shown in Figure 1(b). Formation of clusters on the PANI thin film is noticed at irradiation time 41.00 h, as displayed in Figure 1(c). The density of the formed nanostructures decreases for prolong the irradiation time to 71.00 h, as observed in Figure 1(d).

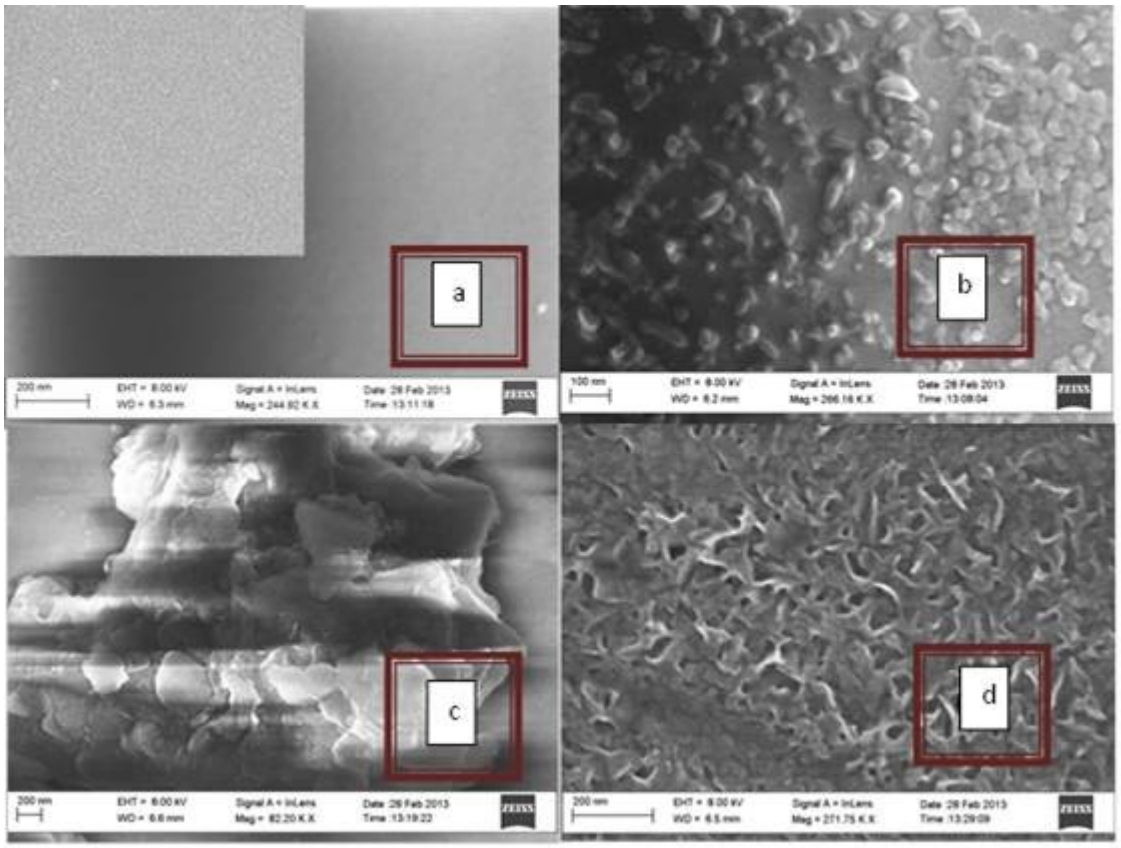

Fig. 1. Top-View FE-SEM images of synthesized PANI samples on glass substrate for virgin and irradiated by alpha particle with different irradiation times: (a) Virgin, (b) 6.50 h, (c) 41.00 h and (d) 71.00 h.

3.2. Optical properties

Irradiation of polymers, undergo main chain scission and cross-linking reactions leading to change the molecular weight products and the surface morphology accompanied with change in optical properties [21]. The optical absorption method can be used for the investigation of the optically induced transitions which can provide information about the band structure and energy gap in crystalline and non-crystalline materials. The UV-VIS spectra of virgin and irradiated PANI samples are shown in Fig. 2. It is clear from the spectra that there is a red shifting in the absorption edge for the irradiated samples from the virgin sample. The red shift indicates a decrease in the band gap after irradiations due to the degradation as a result of bond cleavage in the PANI samples. In addition to, there is a negative correlation between absorbance and the present irradiation times of the alpha particles in the wavelengths range of 530 – 705 nm. It was found that, the correlation coefficient was 0.99 at wavelength, 600 nm. These reflect that the samples after irradiations with the present alpha particle fluences are sensitive to the visible light at the wavelengths 530-705 nm.

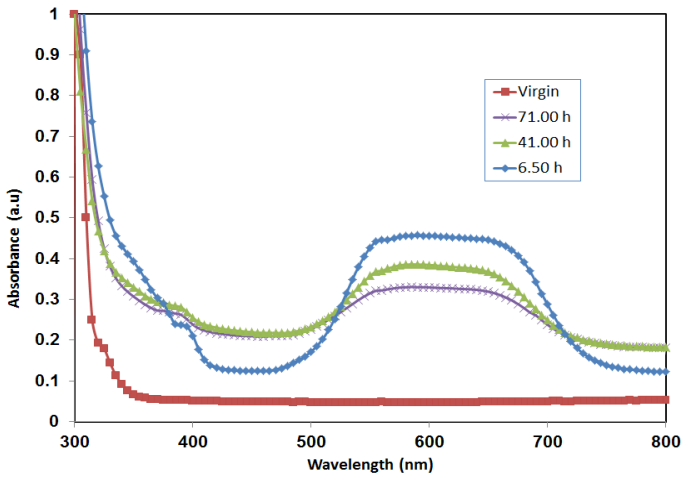

Fig. 2. UV- Vis spectra of the virgin and irradiated of nano-PANI samples with alpha particles at different irradiation times.

The optical band gap energy (E_g) for the PANI samples was calculated from Tauc's expression by the extrapolation of the plot of graph between the photon energy ($h\nu$) and $(\alpha^{\backslash} h\nu)^{1/n}$ for virgin and irradiated PANI samples as shown in Figs.3-6. The Tauc's expression [18] is given by:

$$\alpha^{\backslash}(\nu) = \beta(h\nu - E_g)^n / h\nu \qquad (3)$$

Where β is a constant, $\alpha^{\backslash}$ is the absorption coefficient of the photons in the samples and n is a constant depends on the type of transition. This behavior suggested that the indirect allowed transition (n=2) is the most probable involved transition mechanism. Table I displays the variations of the E_g for the virgin and irradiated PANI samples with alpha particles of different irradiation times. The present study confirmed that the E_g–value for the virgin sample was reduced due to alpha particle irradiations. The variations in E_g suggest formation of defects (radicals and organic species) after alpha particles irradiations and/or the formation of carbon enrich clusters [22]. This may be attributed to the formation of a conjugated system of bonds due to bond cleavage by radiation.

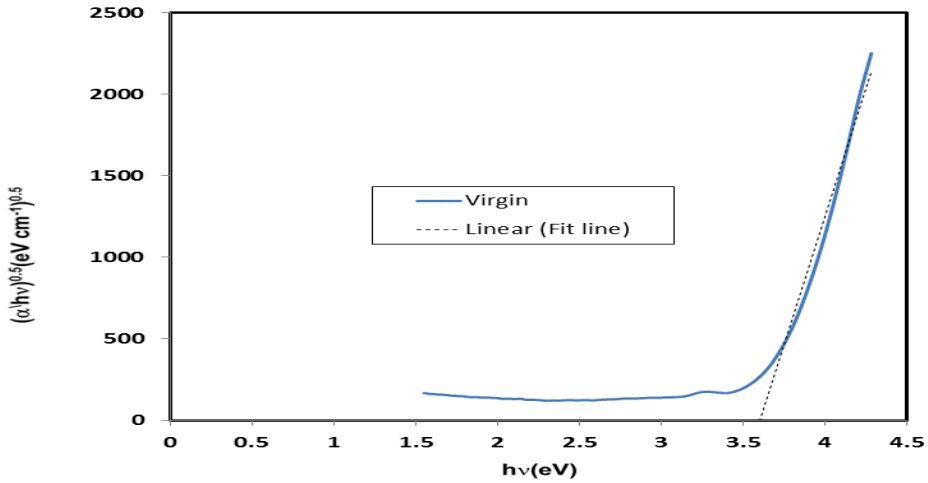

Fig. 3. Tauc's plot corresponding to indirect band gap for virgin PANI sample.

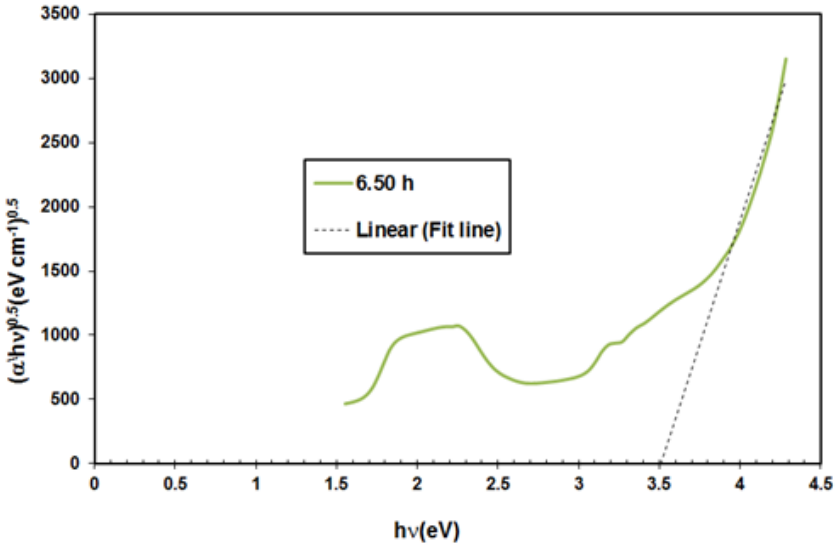

Fig. 4. Tauc's plot corresponding to indirect band gap for irradiated PANI samples at alpha particle irradiation time 6.50 h.

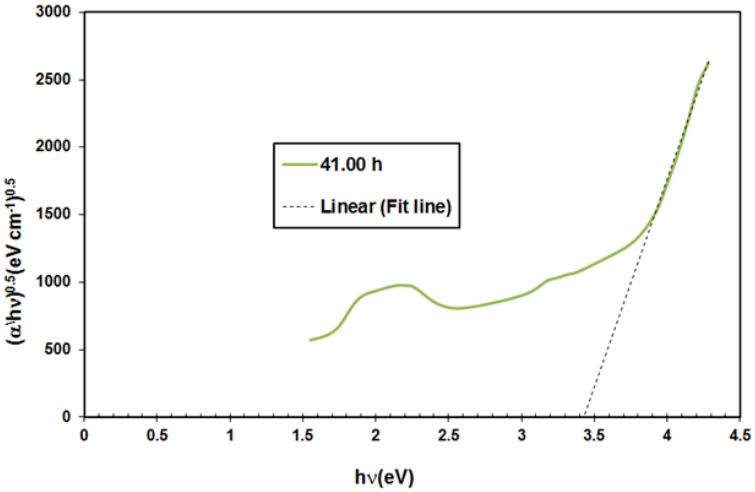

Fig. 5. Tauc's plot corresponding to indirect band gap for irradiated PANI samples at alpha particle irradiation time 41.00 h.

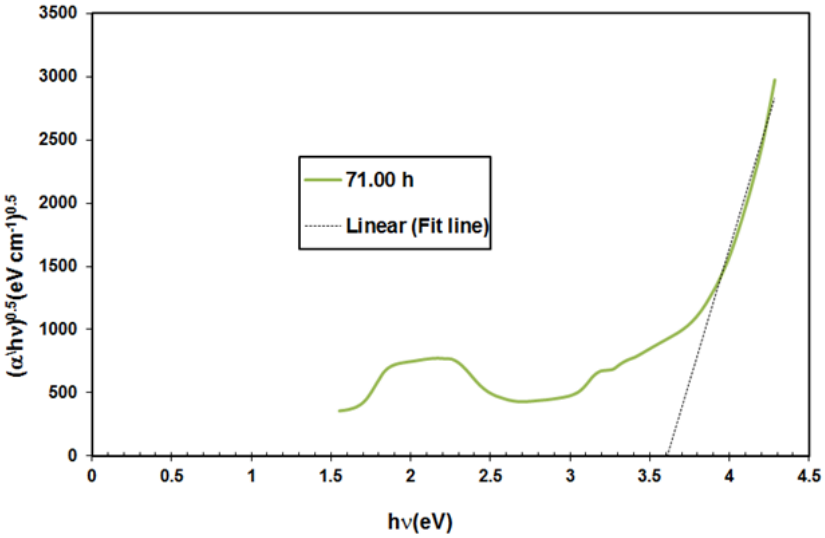

Fig. 6. Tauc's plot corresponding to indirect band gap for irradiated PANI samples at alpha particle irradiation time 71.00 h.

Table I: Variations of the indirect band gap and cluster size for alpha particle virgin and irradiated PANI samples at different irradiation times and fluences

Sample	Fluence (alpha/cm^2)	Indirect band gap energy (eV)	Cluster size
Virgin	**0**	**3.60**	**91**
6.50 h	**1.16 x 10^8**	**3.50**	**96**
41.00 h	**7.48 x 10^8**	**3.42**	**101**
71.00 h	**1.20 x 10^9**	**3.49**	**97**

3.3. Cluster size

The relation between the band gap (E_g) and the cluster size (number of carbon atoms per cluster), N, can be determined according to the following formula [23]:

$$E_g = \frac{34.3}{\sqrt{N}} \text{ eV} \quad (4)$$

The calculated values of N corresponding to the fluence for the virgin and irradiated PANI samples were displayed in Table I. From the Table I one can find that the cluster size for virgin and irradiated PANI varies from 91 to 101 carbon atoms. The maximum value for cluster size was found at irradiation time 41.00 h whereas the minimum value for the band gap energy. This result confirms appearing of clusters in the morphology of the PANI sample at 41.00 h irradiation time as shown in Fig. 1. Carbon enriched domains created in irradiated PANI samples may be responsible for the decreasing in band gap.

IV. Conclusions

The morphology and optical properties of PANI thin film polymer in nanostructure which irradiated with alpha particle at different fluences (1.16 x 10^8 – 1.20 x 10^9 alphas/cm^2) with energy 5.32±0.23 MeV were investigated. The radiation damage is almost regular along the track of alpha particles in PANI samples. The SEM images of irradiated PANI samples, showed the highest number of carbon atoms per cluster were found at irradiation time 41.00 h. The results of the optical properties showed that the samples after irradiations with the present alpha particle fluences are sensitive to the visible light at the wavelengths 530-705 nm. The E_g –value was reduced due to alpha particle irradiations. This may be attributed to the formation of a conjugated system of bonds in PANI films due to bond cleavage by radiation. Also, Carbon enriched domains created in irradiated PANI samples may be responsible for the decreasing in band gap.

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